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THE DETERMINATION OF URANIUM IN ORES, ROCKS AND MINERAL PROCESSING SOLUTIONS BY X-RAY FLUORESCENCE ANALYSIS

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by

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ABSTRACT

The Division of Nuclear Fuel Cycle of the International Atomic Energy Agency has requested the assistance of CANMET in the preparation of a manual on the analytical chemistry of the uranium industry. The staff of the Chemical Laboratory has responded to this request and this report, which deals with the determination of uranium in various matrices, is intended to be part of the manual.

Key Words: Analysis, Uranium, X-Ray Fluorescence, Solutions (Aqueous and Organic), Powders

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LA DÉTERMINATION DE LA PRÉSENCE D'URANIUM DANS DES SOLUTIONS DE TRAITEMENT DES MINERAIS, DES ROCHES ET DES MINÉRAUX PAR L'ANALYSE DE FLUORESCENCE DE RAYONS-X

par

J.L. Dalton* et M. Boncardo**

RÉSUMÉ

La Division du cycle du combustible nucléaire de l'Agence internationale de l'énergie atomique a demandé à CANMET de l'aider à rédiger un manuel sur la chimie analytique de l'industrie de l'uranium. Le personnel du Laboratoire de chimie a répondu à cette demande et le présent rapport, qui porte sur la détermination de la présence de l'uranium dans diverses matrices, doit être intégré au manuel.

Mots clés: Analyse, Uranium, Fluorescence de rayons-X, Solutions (aqueuses et organiques), Poudres

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THE DETERMINATION OF URANIUM IN ORES, ROCKS AND MINERAL PROCESSING SOLUTIONS BY X-RAY FLUORESCENCE ANALYSIS

Uranium has been determined by X-ray fluorescence analysis (XRF) in geological materials (1,2,3), ores (4,5), process solutions (6,7,8), uranium ore concentrates (9,10) and nuclear reactor materials (11,12). As the last two references are not of direct interest to the readers of the manual, they will not be discussed in this chapter.

Wavelength-dispersive spectrometry was used in reference 2,4,5,7,9 and 10 and energy-dispersive in the remainder. In all but one case, the uranium Lα peak was measured. Reference 3 constructed special instrumentation to measure the Kα peak. Calibration techniques varied considerably. Reference 4 simply used a ratio of the net U count rate of the sample to that of a reference material, with a calibration range from 0.01 to 0.25 wt % U_3O_8. Reference 2 used a ratio of the U to the background count rates over a range of 0 to 100 µg/g. Diluton of powdered sample material with elemental sulphur was used by reference 1 to determine uranium and some 39 other elements at the trace level. Reference 4 used the method of standard additions directly on the solids, as well as dissolving the ore sample and analyzing the solutions, using thallium as an internal standard, at 0.2 wt % concentration. A ratio between the U Lα and I Kα incoherent scatter countrates was used by reference 6 over a concentration range from 1 to 500 g/L.

Two preconcentration techniques, ion exchange and precipitation with collection on a silver membrane for references 7 and 8, respectively, were used to determine uranium at 25 µg/g. References 9 and 10 determined uranium in uranium concentrates by dissolving the solid material and analyzing the solution. Calibration was accomplished with a yttrium and strontium internal standards respectively.

The methods described in this article use bromine as an internal standard for the analysis of solutions and tube scattered radiation to compensate for matrix variation for the analysis of solids (13).

ANALYSIS OF AQUEOUS SOLUTIONS USING BROMINE AS AN INTERNAL STANDARD

Instrumentation

Philips PW1400 X-Ray Spectrometer with a PW-1730 X-ray generator, Digital Equipment PDT-1140 programmable data terminal with PW-1400 software used for instrumentation control and data processing, rhodium target X-ray tube operated at 50 Kv 30 mA, fine collimation, air path, lithium fluoride 220 analyzing crystal, uranium Lα measured at 37.26°2Ø with background measurement at 36.26° 2θ with a scintillation detector, Bromine Kα measured at 42.80° 2θ with background measurements at 41.80°2θ and 43.80°2θ with both scintillation detector and flow counter.

Reagents

Uranium Stock Solution: Using NBS 950b pure uranium oxide (14), weigh 0.50 g and transfer to a 250 mL pyrex beaker. Add about 25 mL distilled water, 10 mL of concentrated nitric acid and heat gently. After dissolution, transfer quantititively to a 250 mL volumetric flask and dilute to the mark with water. Prepare several concentrations in the range 0 to 2 g/L by appropriate dilution. 25 mL of each diluted concentration is adequate.

Bromine Internal Standard Solution: 4 mL of concentrated 48% HBr is diluted to 100 mL with distilled water.

Consumables

Polypropylene X-ray cells and rings suitable for use in the PW-1400 spectrometer and Mylar film, 1/4 mil (15).

Calibration

5.0 mL of diluted uranium stock solutions in the range 0 to 2 g/L and 0.10 mL of the bromine internal standard solution are pipetted into a X-ray cell, the cell is covered with the Mylar film and the ring is snapped into place. The cell is then placed into a Philips PW-1220 sample holder, which also has a Mylar window. This assembly is then placed in the PW-1400 sample holder. Measurement times for uranium and bromine peak and backgrounds are 10 and 6 seconds respectively.

The net uranium and bromine counts and the uranium/bromine intensity ratio are obtained and plotted vs concentration. Data from a typical calibration are shown in Table 1. With these conditions, one sigma counting statistics for uranium is 0.7% at the 0.4 g/L concentration and 0.4% for the bromine intensity.

Procedure

Dilute the solution sample to fit the calibration range if necessary. 5.0 mL of sample is transferred to the X-ray cell, 0.1 mL of internal standard is added and the Mylar cover and ring are snapped into place. Proceed with measurement and calculation as described in Calibration. Calculate uranium content by referring the uranium/bromine ratio of the sample to that of the standard solutions.

Comments

The use of bromine as an internal standard will compensate for most compositional changes in the sample solutions. However, if a certain element, or elements, are continually present in high concentrations, then it may be necessary to use that element(s) in the uranium calibration solutions. Bromine intensity responds well to acid changes, as shown in Fig. 1. Significant silver content would prevent the use of bromine, but this is not likely to occur.

Strontium can be used as an internal standard for uranium determination. However, its use is often hindered by the presence of sulphate or phosphate in process solutions.

In most cases, spectral interference is not likely to occur, even with a high thorium and low uranium concentration, for either the uranium or bromine peaks. Some care must be taken to ensure that backgrounds are not taken in the immediate vicinity of the thorium Lα peak at 39.23° 2θ or the bromine Kα peak at 38.24° 2θ.

ANALYSIS OF ORGANIC SOLUTIONS USING BROMINE AS AN INTERNAL STANDARD

The same instrumental parameters are used for organic solutions as for aqueous solutions but the concentration range is reduced to 0 to 1 g/L uranium. The concentration range is reduced because of the limited solubility of the uranium compound chosen for a standard. 2-Bromohexanoic acid is used as internal standard. The same volumes are used, that is 5.0 mL of solution and 0.1 mL of internal standard.

Comments

As with aqueous solutions, the bromine intensity respond to changes in matrix composition. The variation in bromine intensity as a function of volume fraction of tributylphosphate in varsol is shown in Fig. 1.

Reagents

Uranium stock solution: 0.17 g reagent-grade uranyl acetate is weighed, and transferred to a 250 mL pyrex beaker. 10 mL of methanol, 20 mL of versatic acid and approximately 30 mL of varsol are added to the beaker. Heat gently with stirring until dissolution is complete. Transfer to a 100 mL volumetric flask and make up to the mark with Varsol.

Bromine internal standard solution: Dilute 5 mL of reagent-grade 2-bromohexanoic acid to 100 mL with varsol.

Calibration

Prepare several standard solutions with concentrations in the range 0 to 1 g/L U by diluting appropriate quantities of the uranium stock solution. Place 5.0 mL of each standard solution into a X-ray cell and add 0.1 mL of the bromine internal standard solution, cover with Mylar film and snap the ring into place. Use the same parameters for the XRF measurement and subsequent calculations as detailed in the calibration for aqueous solutions analyses.

Procedure

Dilute the organic solution to fit the calibration range, 0 to 1 g/L, if necessary. 5.0 mL of the solution is placed into the X-ray cell, 0.10 mL of the organic bromine internal standard solution is added, the cell is covered with the Mylar film and the ring is snapped into place. Proceed as described in Calibration.

ANALYSIS OF POWDERS USING SCATTERED RADIATION TO COMPENSATE FOR MATRIX VARIATIONS

X-Ray Fluorescence intensities are influenced significantly by the sample matrix (2). The scattered radiation from the X-ray tube may be used to compensate for both physical and chemical variations, as it is sensitive to changes in average atomic number, density and grain size (16). Calibration is achieved by plotting the ratio of the uranium net counts to the scatter net counts versus the uranium concentration.

An important variable that should be controlled, if possible, is that of grain-size distribution. This variable may be controlled if all powder samples are ground in the analytical laboratory using the same grinding apparatus with the same conditions. It has been reported that grinding apparatus has its own characteristics and will produce a characteristic grain-size distribution (17). This particular distribution, in turn, has a direct influence on X-ray intensities (18,19). While the scatter correction will compensate for some changes in grain size, control of this variable is recommended.

It is also recommended that separate calibrations are established for each type of sample, such as geological, mine, mill heads, tails, etc., to minimize matrix variations within a particular calibration. A problem with this practice, however, is that it may be difficult to obtain a suitable calibration range with just one type of sample. Hence, the reason for referring to the scatter as a matrix variation correction, so that a single calibration may be used for more than one type of material.

The calibration described later used material from two different Canadian ore-bodies and this was used to determine uranium in Canadian tailings, American ore-grade and Chinese geological materials. All of the material shown in Table 2 are available from the Canadian Certified Reference Materials Project (20) except the Chinese materials (21).

Instrumentation

- Suitable grinding apparatus such as a Shatterbox (15).
- Suitable pellet press such as the Herzog (22).
- Philips PW-1400 X-Ray Spectrometer. The instrument parameters are

the same as for the analysis of solutions except for the following differences: rhodium target X-ray tube operated at 50 Kv 50 mA, rhodium scatter peak measured at 26.28° 2θ and backgrounds at 24.28 and 28.08° 2θ with the scintillation detector, measurement times for both uranium peak and rhodium scatter peaks were 10 seconds and backgrounds were 6 seconds. Air path.

Consumables

Aluminium sample cups suitable for use in the PW-1400 spectrometer (15).

Procedure

The material should be ground in the grinding mill until the desired grain-size distribution is obtained. The criteria should be that 100% of the powder will pass through as 74μm sieve (200 mesh). The CCRMP reference materials are typically 100% minus 74μm and some 70% less than 37μm size (400 mesh) (20).

The ground material is either used for the preparation of a pressed powder pellet or simply placed into an X-ray cell. If a pressed powder pellet is used, the materials is placed in the aluminium cup and tapped firmly several times after each addition. The cup is filled almost to the rim and then placed in the pellet press and pressed at a suitable pressure for approximately 100 seconds. The benefits to using a pressed powder pellet are a constant density and the possible use of a vacuum path.

If the polypropylene cell is used, enough material is placed in the cell to almost fill it, covered with Mylar film and the ring snapped into place. The cell is then placed directly into the PW-1400 sample holder.

The XRF measurements are made with the parameters detailed in Instrumentation.

A ratio is calculated for the net uranium to the net scatter counts and this is plotted against wt % uranium in the reference materials. Sample ratios are referred to this plot to obtain the uranium concentration.

Data from a typical calibration are shown in Table 2. The column headed 'Calculated' lists the results calculated by the linear regression equation produced by data from the reference materials denoted with an asterisk. A perusal of this data suggests that the accuracy of the method

is generally within ± 10% of the certified value, but there are some exceptions. The regression data shows the advantage of using the scattered radiation to compensate for matrix variation. The correlation coefficient from the ratio data indicates less scatter than with using only the uranium countrate.

Table 1 - Calibration Data
Determination of Uranium in Aqueous Solutions

Solution	Composition (g/L)			IU cps	I_{Br} cps	I_U/I_{Br}	U Concentration (g/L)	
	Fe	S	Ca				Sought	Calculated from regression
	⟵	g/L	⟶					
Std A*	-	-	-	5876	4498	1.3066	2.00	1.98
B*	-	-	-	3176	4811	0.6602	1.00	1.01
C*	-	-	-	1257	4830	0.2603	0.40	0.40
D*	-	-	-	118	5201	0.0227	0.04	0.046
1	3.0	3.0	3.0	62	2614	0.0239	0.04	0.045
2	3.0	3.0	3.0	42	3891	0.0108	0.02	0.022
3	3.0	3.0	3.0	258	3829	0.0674	0.10	0.107
4	6.0	1.0	1.0	932	3406	0.2736	0.40	0.424
5	1.0	2.0	2.0	3005	4451	0.6752	1.00	1.03
6	0.5	2.0	2.0	2875	4340	0.6625	1.00	1.01
7	0.4	0.8	0.8	4739	4501	1.0529	1.60	1.59
8	5.0	-	-	2497	3705	0.6741	1.00	1.03
10	-	-	5.0	2735	4143	0.6602	1.00	1.01
11	-	2.0	-	3036	4569	0.6647	1.00	1.02
12	0.5	2.0	5.0	2938	4338	0.6773	1.00	1.01

* solutions used for calibration

Table 2 - Calibration Data
Determination of Uranium in Powdered Samples

Material	Source	I_U cps	I_{Rh} cps	I_U/I_{Rh}	Uranium wt % Certified	Uranium wt % Calculated from regression
DH-1*	Canada	1803	2122	0.8487	0.177	0.175
UTS-1	Canada	33	2130	0.0153	0.0049	0.005
UTS-2	Canada	51	2750	0.0186	0.0056	0.006
UTS-3	Canada	655	2658	0.2464	0.0513	0.052
UTS-4	Canada	1701	3029	0.5620	0.1010	0.117
BL-2A*	Canada	4679	2251	2.0787	0.426	0.425
BL-3*	Canada	10256	1940	5.2877	1.02	1.077
BL-4A*	Canada	1580	2412	0.6550	0.1248	0.136
CUP-1	U.S.A.	1295	1763	0.7344	0.128	0.152
EJ-177	China	406	2168	0.1875	0.0285	0.031
EJ-178	China	1418	3112	0.4555	0.0788	0.095
EJ-179	China	1079	2932	0.3680	0.0682	0.077
EJ-180	China	2356	2802	0.8409	0.194	0.173
EJ-181	China	9115	2308	3.9495	0.703	0.805
EJ-182	China	997	1790	0.5573	0.0986	0.115
EJ-183	China	164	510	0.0167	0.0536	0.066
DH-1A*	Canada	2539	2216	1.1459	0.2629	0.235
DL-1	Canada	52	3280	0.0159	0.0041	0.006
DL-1A*	Canada	164	3190	0.0513	0.0116	0.013

* materials used for calibration

Linear Regression Data

	IU vs Uranium wt %	I_U/I_{Rh} vs Uranium wt %
slope	10,795.267262	5.261033
intercept	81.424120	0.041262
correlation coefficient	0.986520	0.995703

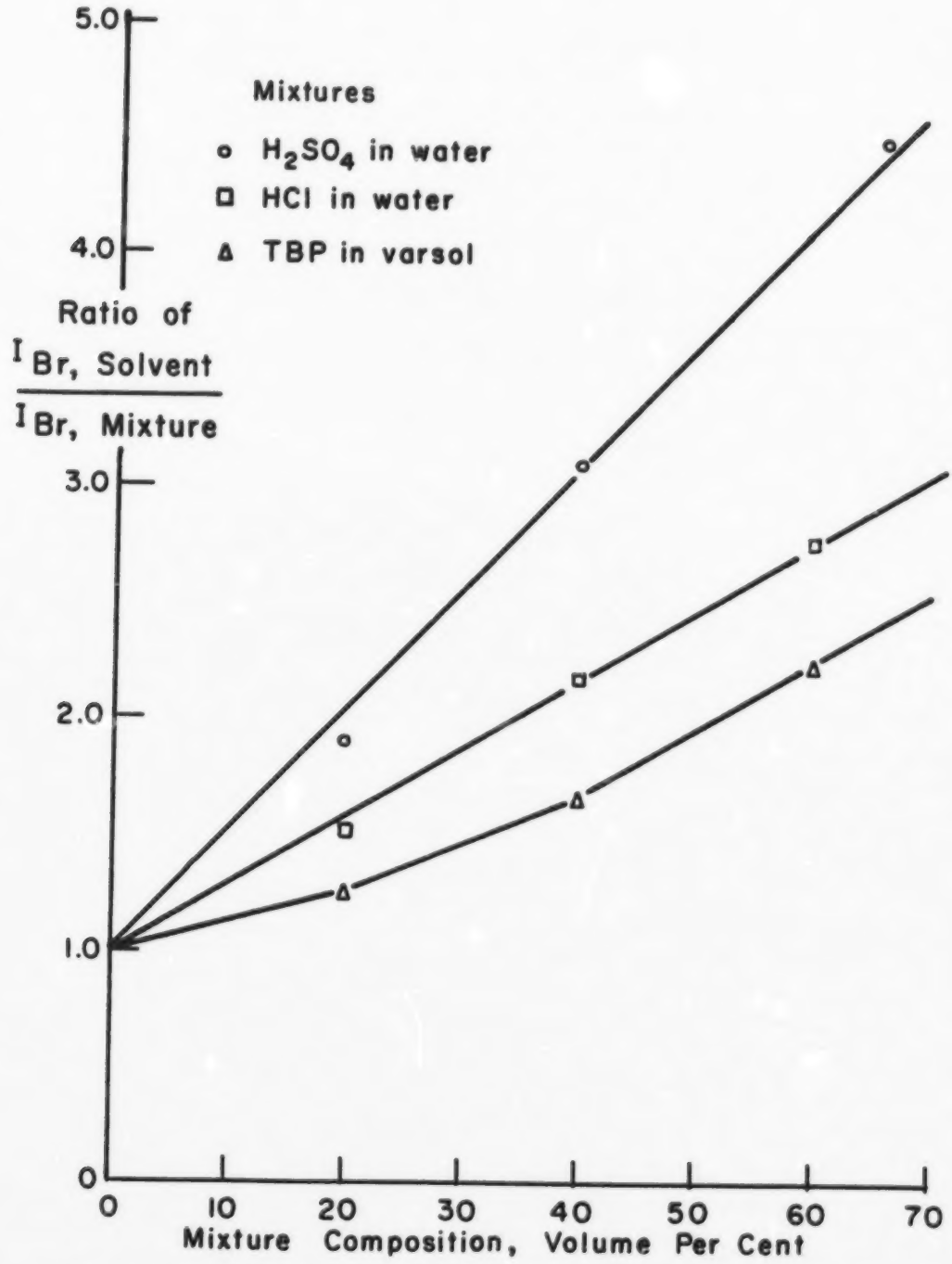

Fig. 1 - Effect of Solution Mixture on Br $K\alpha$ Intensity

REFERENCES

1. Giauque, R.D., Garrett, R.B, Goda, L.Y., "Determination of forty elements in geochemical samples and coal fly ash by X-ray fluorescence spectrometry", Anal. Chem. 49, 1012-1017, 1977.

2. James, C.W., "Parts-per-Million determination of uranium and thorium in geologic samples by X-ray spectrometry", Anal. Chem. 49, 967-968, 1977.

3. Kumpulainen, H., "Uranium analysis by K X-rays from geological samples", J. Radioanal. Chem. 59, 635-640, 1980.

4. Philips Bulletin, "Use of the PW-1250 for the analysis of uranium ores", Scientific and Analytical Equipment Department, N.V. Philips Gloeilampenfabricken, Eindhoven, The Netherlands, 79.177/FS11.

5. Zimmerman, J.B., "The determination of rranium in ores from Denison and Beaverlodge mines by X-ray fluorescence spectrometry", Extraction Metallurgy Division, Divisional Report EMT 71-4, CANMET, Energy, Mines and Resources, Canada.

6. Shenberg, C., and Amiel, Saadia, "Analytical significance of peaks and peak ratios in X-ray fluorescence analysis using a high resolution semiconductor detector", Anal. Chem. 43, 1025-1030, 1971.

7. Jablonski, B.B. and Legden, D.E., "X-ray fluorescence determination of uranium as the barium diuronate precipitate", Anal. Chem. 51, 681-683, 1979.

8. Feldstein, H. and Gilath, I., "Determination of low uranium concentration in carbonate-bicarbonate solutions by X-ray fluorescence", J. Radioanal. Chem. 57, 47-52, 1980.

9. Jensen, C.L., and Baur, G.S., "Determination of uranium in high-grade uranium concentrates by an X-ray emission spectrographic method", Appl. Spectroscopy, 26, 57-59, 1972.

10. Donahue, B., "The determination of uranium in high-grade chemical precipitates by X-ray spectyrometry", Proc. Third Annual Meeting, Canadian Mineral Analysts, 1971.

11. Dragnev, T.N., Karamanova, J., And Damianov, B., "Precise ion destructive X-ray fluorescence method for uranium and thorium concentration measurements", J. Radioanal. Chem. 52, 439-448, 1979.

12. Berdikov, V.V.., Grigorev, O.I. and Ioklin, B.S., "X-ray fluorescence determination of uranium and neighboring elements in solution", J. Radioanal. Chem. 68, 181-192, 1982.

13. Dalton, J.L., Unpublished Results, CANMET, Energy, Mines and Resources, Canada, Ottawa.

14. Reference Material 950b, United States Dept. of Commerce, National Bureau of Standards, Washington, D.C.

15. Spex Industries, Inc., Metuchen, N.J., U.S.A.

16. Andermann, G. and Kemp. J.W., "Scattered x-rays as internal standards in X-ray emission spectrometry", Anal. Chem., 30, 1306-1309, 1958.

17. Alcock, A.R., "Rapid X-ray analysis of geological samples", Geoanalysis 78 Symposium, 1978, Energy, Mines and Resources Canada, Geological Survey of Canada.

18. Claisse, W., "Overcoming the particle size effice in the internal standard method of X-ray fluorescence analysis", Spectrochem. Acta. 25B, 209-218, 1970.

19. Lubecki, A., Holynska, B., and Wasilewska, M., "Grain size effect in non-dispersive X-ray fluorescence analysis", Spectrochem. Acta 23B, 465-470, 1968.

20. Canadian Certified Reference Materials Project, Energy, Mines and Resources Canada, CANMET, Ottawa, Canada, K1A 0G1.

21. Yang, Z. and Lia, X., "Seven standard ore samples of uranium, thorium and radium by the Bureau of Uranium Geology", Geostandards Newsletter, VII, 251-260, 1983.

22. Scientific and Equipment Division, Philips Electronics Ltd., Scarborough, Ontario, Canada, M1B 1M8.